

Chapter 2

Continuous Monitoring of Ozone

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1.0 Introduction

It is the intent of this chapter to outline the requirements for the ambient air monitoring of ozone (O_3). All agencies or groups that conduct ozone monitoring within the state of Indiana and submit data to the Air Quality System (AQS) database must follow requirements in this chapter. Indiana's ozone monitoring season is April 1 through September 30.

The United States Environmental Protection Agency (USEPA) has established a new national ambient air quality standard (NAAQS) for ozone. The USEPA is phasing out and replacing the previous 1-hour primary standard with a new 8-hour standard. **The new standard is defined as the 3-year average of the annual 4th highest daily maximum 8-hour ozone concentrations not exceeding 0.08 parts per million (ppm). By using conventional rounding, the concentration must not exceed 85 parts per billion (ppb).** The new standard will provide increased protection to the public; especially children and other at-risk populations, against a wide range of O_3 induced health effects. Some of these health effects include decreased lung function, increased respiratory symptoms, inflammation of the lung, and possible long-term damage to the lungs. The previous standard of 0.12 ppm for 1-hour will still be in place until data from a given area is reviewed and found to meet the 1-hour standard. This is to ensure a smooth transition to the new standard. USEPA also replaced the secondary standard (to protect agricultural crops, national parks, and forests) with a standard identical to the new primary standard.

2.0 Probe Siting Criteria

For specific siting requirements for O_3 monitors and inlet probes, refer to Chapter 1 of this manual and to the Code of Federal Regulations (CFR) 40, Part 58, Appendixes D and E.

2.1 Horizontal and Vertical Probe Placement

- The inlet probe must be 3-15 meters above ground level.
- If on the side of a building, it must be on the windward side relative to the prevailing seasonal wind.
- It must be 1 meter vertically and horizontally away from any supporting structure and away from dusty areas.

2.2 Spacing from Obstructions

- If on a rooftop, it must be at least 1 meter from walls, penthouses, etc.
- The distance between obstructions and the inlet probe must be at least twice the height the obstruction protrudes above the inlet port.

- Airflow must be unrestricted in an arc of at least 270° around the probe and the predominant seasonal wind direction must be included in that arc.
- If the probe is located on the side of a building, 180° clearance is required.

2.3 Spacing from Roads

It is important to minimize the destructive interferences of nitric oxide (NO) since NO readily reacts with O₃ (see Table 2-1 for separation distances between roadways and stations).

2.4 Spacing from Trees

Since the scavenging effect of trees is greater for O₃ than for other priority pollutants, strong consideration must be given to the location of an O₃ inlet probe. Therefore, the sample probe must be at least 10 meters from the drip line of trees which are located in the predominant seasonal wind direction. Generally, the probe should be at least 20 meters from the drip line of trees in all directions.

Table 1
Minimum Separation Distance Between Neighborhood and Urban Scale
Ozone Stations and Roadways

Average Vehicles per day	Minimum Separation (meters) *
less than 10,000	greater than 10
15,000	20
20,000	30
40,000	50
70,000	100
less than 110,000	greater than 150

* Distances should be interpolated based on traffic flow.

3.0 Monitoring Methodology

All methods used to monitor O₃ must be a reference method or equivalent procedure described in 40 CFR Part 53. For all analyzers, refer to the manufacturer's instruction manual for analyzer-specific requirements.

3.1 Ultraviolet (UV) Absorption Method

This method used to monitor O₃ is based on the principle that O₃ absorbs ultraviolet light. The greatest absorbance takes place at the 253.7 nm wavelength. A low pressure mercury vapor

lamp produces light at this wavelength. This light is admitted into a measuring cell. Ozonated (sample) air and non-ozonated (zero) air are alternately passed through the sample cell. This provides a continuous reference so that any variation in lamp intensity can be accounted for.

Monitoring Requirements (include but are not limited to):

- The sample manifold and all contact sample lines and connectors must be borosilicate glass or Teflon.
- The analyzer reads mercury vapor as ozone, therefore the analyzer should not be placed in a facility where mercury contamination is possible (i.e. laboratories).
- Airflow to the monitoring system should be unrestricted.
- The incoming sample air should not be pressurized.
- UV lamp must be working properly. CAUTION: Ultraviolet light can cause damage to the eye. Never inspect without protective equipment (glass or plastic lenses may not filter out UV light).

4.0 Calibration Methodology

The Office of Air Quality's (OAQ) primary standard photometer is certified, by the U.S. EPA Region 5 facility one time a year prior to ozone season by comparing it to their Standard Reference Photometer. Field calibrations are performed using transfer standards certified against the OAQ primary standard. Calibrations must follow the criteria established in 40 CFR Part 50, Appendix D.

Calibrations and audits should be carried out at the field monitoring site by allowing the analyzer to sample test atmospheres containing known pollutant concentrations. The analyzer to be calibrated should be in operation for at least several hours (preferably overnight) prior to the calibration so that it is fully warmed up and its operation has stabilized. During the calibration, the analyzer should be operated in its normal sampling mode, and it should sample the test atmosphere through all filters, scrubbers, conditioners, and any other components used during normal ambient sampling and through as much of the ambient air inlet system as possible.

There are two types of calibrations, a multi-point calibration and a Level 1 calibration. A multi-point calibration consists of three or more test concentrations, which includes a zero concentration (pollutant free air), a concentration between 80% and 90% of the full scale range of the analyzer being calibrated, and one or more intermediate concentrations spaced approximately equally over the scale range. This multi-point calibration should be performed at the time of initial installation. A Level 1 calibration consists of a two point analyzer calibration (zero and span only) which should be used when the analyzer's linearity does not need to be checked.

A multi-point calibration of an analyzer must be performed if any of the following conditions exist:

1. A six (6) month period has lapsed since the most recent multi-point calibration.
2. If all calibration points are not within $\pm 2\%$ of the full range of the monitor (e.g., if the range is 0.5 ppm, then all measured values must be within .010 ppm of the standard).

A Level 1 calibration of an analyzer must be performed if any of the following conditions exist (the multi-point can always substitute for the Level 1 calibration):

1. After an interruption of more than 24 hours of operation
2. Any repairs which may affect calibration, e.g.
 - a. Replacement of electronic boards
 - b. Replacement of any optics (mirrors)
 - c. Replacement of solenoid switching valves
3. Physical relocation of the analyzer
4. Any other indication of possible significant inaccuracy of the analyzer
5. If all calibrations points are not within $\pm 2\%$ of the full range of the analyzer (e.g., if the range is 0.5 ppm, then the measured values must be within ± 0.010 ppm of the standard. Therefore, if the standard concentration introduced into the analyzer is .400 ppm, the measured value must be between .390 and .410 ppm).

4.1 Determination of Concentration

Use the following formula to determine O₃ concentrations:

$$\text{Standard Concentration} = 1/\text{slope} \times (\text{Indicated O}_3 \text{ Value} - \text{Intercept})$$

The slope and intercept are determined during the certification of the calibrator. See Chapter 6 of this manual for the certification procedures.

4.2 Calibration Requirements (include but are not limited to the following):

- O₃ calibration system (generator) must have ample warm up time prior to use (usually 15 to 30 minutes).
- Dilution air must be dry, free of nitrogen oxides, ambient O₃, and traces of mercury.

4.3 Certification Requirements

IDEM/OAQ/QAS certifies ozone transfer standards every three months using the OAQ primary standard photometer. The transfer standard can be certified once per six months if fixed at a site and it shows good stability. If a transfer standard is to be used to certify other ozone transfer standards, it is considered a primary standard. Therefore, Chapter 6, Section 5 must be used as a guideline for certifications. In addition, IDEM/OAQ/QAS may be notified to obtain the Technical Assistance Document EPA-600/4-79-056. See Chapter 6 of this manual for more specific information on transfer standards.

5.0 Calibration Procedure

The procedures outlined below are general. Always refer to the manufacturer's instruction manual for analyzer-specific alterations or explanations.

5.1 Record Keeping

A calibration worksheet should be completed with each calibration (see Form 1). If using a generic form, the following information must be included:

- official site name (include AQS#)
- instrumentation identification (include manufacturer's name, model, and serial numbers)
- identification of person performing the calibration
- date of calibration
- calibrator identification (include manufacturer's name, model, and serial numbers)
- calibrator certification date
- standard concentration
- analyzer's air flow, vacuum pressure, initial and final zero and span potentiometer settings
- initial and final time (of the calibration)
- temperature at the site in degrees Celsius
- measured responses

The primary and secondary recording units and the station logbook must also be labeled with the information listed below to avoid any confusion when the raw data is reduced:

- site identification
- initials of person performing the calibration
- parameter (O₃)
- start/stop time, date
- identification of operation (calibration, audit, etc.)
- results

5.2 Calibration Process

A data validation audit should be conducted prior to any routine recalibration. This one point audit must be conducted prior to any analyzer adjustments. The purpose of the audit is to determine the validity of the data from the last audit or calibration to the present date. See Section 6.0 for the audit procedures.

Observe the following steps when performing a multi-point calibration on a UV absorption ozone monitor:

1. Attach the analyzer's sample line to the vented output of the calibrator. A vented output consists of a union tee to bleed off excess pressure or an output manifold on the calibrator. **If excess flow pressure is not released, the analyzer could be damaged.** Adjust the zero air flow from the calibrator to the analyzer. The zero air flow must exceed the analyzer's total flow demand by at least 25% to ensure that no ambient air is pulled into the system through the vent. For example, if the analyzer flow demand is 1.0 L/min then the total output flow from the calibrator should be no less than 1.25 L/min.
2. Allow for stabilization (a response is considered stable when the display does not vary more than 5 ppb over a five minute period). Using the analyzer's zero adjustment, adjust the analyzer response to read .000 mV or ppm on the data acquisition system. Offset the back-up chart recorder by + 5% to track negative zero drift. Record the responses on the calibration worksheet.
3. Using the O₃ standard concentration equation (Equation 2-1) accompanying the certified ozone generator or photometer, determine the calibrator settings required to generate a concentration at approximately 80% of the analyzer's range (e.g., for an analyzer operating in the 0-0.5 ppm range, .400 to .450 ppm should be used as the span concentration).

Equation 2-1

$$\text{Std. Conc. (ppm)} = \text{Slope} \times (\text{indicated O}_3 - \text{intercept})$$

Allow the analyzer to sample until the response is stable. Adjust the span adjustment until the response on the primary recorder matches the standard concentration determined in Equation 2-1 within $\pm 2\%$.

4. If the span is adjusted, recheck the zero and span by repeating steps 2 through 5.
5. After the zero and the 80% of range concentration have been set (.400 to .450 ppm), make no further adjustments with the zero or span controls. One additional, concentration must be introduced (e.g. .180 to .220 ppm is an ideal range). Record the standard concentrations (those introduced by the O₃ generator or photometer) and the analyzer's indicated response to those points on the calibration worksheet.

6. Determine the calibration slope using the least squares linear regression method to find the line of best fit. Using Equation 2-2, convert the analyzer responses (observed concentration) from millivolts, volts, or percent chart to ppm and use these concentrations as the X values. Use the standard ozone concentrations (generated from a certified ozone generator or photometer) in ppm as Y values. Calculate the measured concentration using the observed concentrations and the calibration slope and intercept. Compare the difference between the measured and standard concentrations. Repeat any points falling outside $\pm 2\%$ of the range of the monitor (**e.g., if the range is 0.5 ppm, then all measured values must be within .010 ppm of the standard**). If the repeated points are still outside the 2.0% limit, the calibration is considered invalid. If a successful calibration cannot be completed in two attempts, the instrument is considered suspect, and maintenance may be required.

OR

7. Adjust the analyzer's span pot so that the slope is a fixed value (i.e., for a 0.5 ppm range: a 0.5 slope for a 1 volt output; a 0.005 for a 100 millivolt or strip chart output; a 0.0005 slope for a 1000 millivolt).

This method will allow the same slope for data reduction to be used for the entire network. All calibration concentrations must be within $\pm 2\%$ of the range of the monitor.

Equation 2-2

$$\text{Analyzer Observed Concentration} = (\text{Analyzer Response} - \text{Zero Response}) \times \text{Slope (of calibration)}$$

The example calculation below assumes a 1000 millivolt range data acquisition system:
(870 mV - 30 mV) x .0005(Slope) = .420 ppm (Observed Conc.)

5.3 Calibration Frequency

To ensure accurate ozone measurements, calibrate each analyzer at the time of initial installation:

- Recalibrate no later than six months after the most recent calibration, using the multi-point calibration procedures in Section 5.2.
- Recalibrate if one of the following conditions is met:
 1. An interruption of more than 24 hours of the sampler's operation
 2. Any major repairs such as replacing boards, photometer tubes, etc.
 3. Accidental contamination of the system with mercury or mercury vapors
 4. Physical relocation of the unit

5. Any performance audit failure or excessive zero/span drift. See Chapter 11 of this manual for zero/span drift limitations, and Section 6.0 below for audit failure procedure and limits.

A zero/span check (Level 2) may be used to determine if a calibration is necessary should conditions listed above occur see (Section 8.5). However, a Level 2 check may not be substituted for a required six month multi-point or Level 1 calibration.

6.0 Quality Assurance Audits

Quality assurance audits are performed to ensure the validity of the data submitted. Results of these audits are also used to calculate the Precision and Accuracy (P&A) of a monitor or network. The Quality Assurance Section (QAS) submits quarterly reports of the statewide P&A data to U.S. EPA through the Air Quality System database (AQS). See Chapter 13 of this manual for specific instructions on how to calculate and report P&A values.

All continuous ozone analyzers are audited every **two weeks** during season of operation. Indiana's ozone season runs from April 1 through September 30. Each audit consists of two phases, a precision check and a data validation check. These precision and data validation checks are done in addition to three (3) or four (4) point accuracy audits (see performance check for each respective monitor) which are performed at least once per quarter.

6.1 Precision Audit and Data Validation

Precision audits must be performed on each analyzer in a monitoring network. Using the method outlined in Section 5.2 of this chapter, introduce an O₃ concentration from each of the concentration ranges listed below. These concentrations are for analyzers that operate in the 0.5 ppm range. **MAKE NO ADJUSTMENTS TO THE ANALYZER.**

Monitors Ranging from:	Concentrations:
0 - .500 ppm	.350 - .450 ppm Validation pt.
	.080 - .100 ppm Precision pt.

6.1.1 Calculation of Results

Using Equation 2-3, calculate the percent difference between the standard and observed concentration in the data validation range. If the percent difference is less than or equal to 7.5%, then the data for the operational period (the date of the last audit or calibration to the date of the current audit) is valid and the monitor does not require recalibration.

Equation 2-3

$$\% \text{ Diff.} = \frac{\text{Observed Conc.} - \text{Standard Conc.}}{\text{Standard Conc.}} \times 100$$

$$\text{Example calculation: } \frac{.420 - .400}{.400} \times 100 = 5.0\%$$

If the percent difference is greater than $\pm 7.5\%$ and less than or equal to $\pm 15.0\%$, the data is valid but the monitor is out of calibration and should be recalibrated as soon as possible.

If the percent difference is greater than 15.0% , the data for the operational period is invalid and the monitor must be recalibrated.

If the spread of the percent difference is $\geq 10\%$ between any two audit points or if the percent difference of any individual point is $\geq 10\%$, QAS recommends that the auditor investigate for problems with the analyzer.

6.1.2 Audit Instrumentation

Precision and data validation audits may be performed using any currently QAS certified, operational system. See Chapter 6 of this manual for certification requirements.

6.1.3 Record Keeping

- Record all audit information on the audit worksheet (see Form 2), keep worksheets on file in the network office off the site, and give a copy to the operator;
- Record pertinent information in the site logbook such as the percent differences, flows, zeros, etc.

6.2 Accuracy Audit

Accuracy audits must be performed on 25% of the reporting organization's ozone sites each quarter such that each analyzer is audited at least once per year. If there are fewer than four analyzers within a reporting organization, randomly reaudit one or more analyzers so that at least one analyzer is audited each calendar quarter (40 CFR Part 58, Appendix A). However, the IDEM/OAQ/QAS strongly encourages more frequent auditing (once each quarter per analyzer is recommended). Accuracy audits are submitted for valid data only. Using the method outlined in Section 5.2 of this chapter, introduce an O_3 concentration from each of the concentration ranges listed below. These concentrations are for analyzers that operate in the 0.5 ppm range. **MAKE NO ADJUSTMENTS TO THE ANALYZER.**

Monitors ranging from:	Concentrations:
0-.500 ppm	.030 - .080 ppm (Level 1)
	.150 - .200 ppm (Level 2)
	.350 - .450 ppm (Level 3)

6.2.1 Audit Results

See 6.1.1. of this chapter for calculations. The Level 3 percent difference is subject to the requirements of Section 6.1.1.

6.2.2 Audit Instrumentation

Accuracy audits must be performed using a different system than the one used to calibrate.

- The auditor should be someone other than the primary operator.
- The auditing system used must be currently certified. See Chapter 6 of this manual for certification requirements.

6.2.3 Record Keeping

- Record all information on the accuracy audit worksheet (see Form 2). Retain these worksheets at the network office and give a copy to the operator;
- Record pertinent information in the station logbook such as the percent differences, flows, zeros, etc.

7.0 Data Reduction and Reporting

The NAAQS for ozone is based on measured hourly average concentrations. Therefore, the data submitted to the State for entry into the AQS system must be reduced to hourly average concentrations daily. This reduction must be done manually in networks not equipped with electronic averaging instrumentation. See Chapter 12 of this manual for the procedures and quality assurance requirements for data reduction. Data should be submitted to the IDEM by the 15th of the following month to allow sufficient time for review before National Air Data Branch (NADB) deadlines (within 45 days after the end of the reporting period).

8.0 Routine Station Operation

Essential to the quality assurance program are scheduled checks for verifying the validity of the monitoring system. At least once each week, the network operator should visit each site to physically determine the operating conditions. A site check sheet should be filled out during each weekly visit.

8.1 Shelter Temperature

Mean shelter temperature should be between 20° and 30° C. A certified thermograph or other temperature recording device should be installed at the site to continuously monitor the daily temperature fluctuations. Data may be invalidated anytime the shelter temperature exceeds 33°C or falls below 15°C (40 CFR Part 53.31 (a)).

8.2 Sampling Station

The following components should be inspected weekly for breakage, leaks, and buildup of particulate matter or moisture:

- sample intake port
- particulate and moisture traps (change or empty as needed)
- sampling manifold and blower
- sampling line to the analyzer

8.3 Recording Device

Whether utilizing a computer printout, a strip chart, or both, check the following weekly:

- ink trace or printout for legibility
- ink or ribbon reservoir
- paper supply
- time synchronization
- computer status

8.4 Analyzer Visual Checks

The field operator should check weekly the operating parameters of the analyzer. Record these and other pertinent observations on a check sheet. These will vary from instrument to instrument but in general will include:

- correct settings on flow meters and regulators
- verification of sample mode
- zero and span potentiometers set and locked
- abnormal electronic noise or temperature

8.5 Zero/Span Checks

Zero/Span checks are recommended daily. A zero and 70 - 90% of analyzer range concentration check should be performed on each analyzer within a reporting network. Many instruments are equipped with an internal or automatic capacity to cycle through a zero/span each day.

If an instrument does not have this capacity, this zero/span must be done manually at least once per week. If the analyzer drifts excessively, more frequent zeros and spans will be required. Although not used specifically for data validation/invalidation, it does help to track a monitor's drift pattern and may show at what particular point a monitor began to show a trend. If an audit exceeds the allowed percent difference and records of zero/span checks can be supplied to identify when excessive drift began, it may not be necessary to invalidate an entire operational period. Decisions on data validation are made by the QA Section Chief. See Chapter 11 of this manual for zero/span drift limits.

9.0 Preventive Maintenance

Analyzers must have routine preventive maintenance performed to ensure proper operation. Most manufacturers supply a preventive maintenance check list with the instruction manual. An analyzer-specific schedule, similar to that shown below should be located at each site, and all maintenance should be recorded in the station logbook.

Sample Preventive Maintenance Schedule

Item	Action Required	Date Due	Date Performed	Next Date Due
Particulate Filter	Change	06/06/05	06/08/05	06/22/05
Pump Diaphragm	Change	06/01/05	06/01/05	12/01/05
Fan Filter	Examine	06/01/05	06/01/05	07/01/05
Span Cylinder	Check	Weekly		
Fitting	Check	Weekly		
etc.				

Form 1 **Ozone Calibration**

Site:		AQS #:	
Data Status:			
Date:		Performed by:	
Start time:		End time:	

Analyzer Information

Brand/Model:		S.N.:	
Range: 0 to		ppm	Slope

Calibrator Information

Brand /Model		S.N.:	
Certification Date:		Standard Conc. =	*(Indicated O ₃ Value -)

Calibration Data:

Primary Recording Device:		S.N.:		Units:	
Secondary Recording Device:		S.N.:		Units:	

Initial Zeros:

Primary Response:		Secondary Response:		DVM response:	
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O₃ Audit Information

Calib. Settings	Calib. (in ppb)	Monitor response			Measured conc. (in ppm)	Standard conc. (in ppm)	% Diff.	
		DVM Units:	Primary Units:	Secondary Units:			Primary	Secondary

Audit pot information:

Zero Pot:		Span Pot:	
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Ozone Calibration Information

Calib. Settings	Calib. (in ppb)	Monitor response			Measured conc. (in ppm)	Standard conc. (in ppm)	% Diff.	
		DVM Units:	Primary Units:	Secondary Units:			Primary	Secondary

Calibration pot information:

Zero Pot: Span Pot:

For TECO Only:

A/B Test:

Are the 10 averages within 3.0% ? : (Circle one) Yes No

Leak Test: Site Temp: Reminder: IS PSI SET IN COMPUTER?

DIAGNOSTICS

TECO										DASIBI	
Flow:	A:				B:				Flow:		
For 49:											
Noise:	A:				B:				Sample Frequency:		
Frequency	A:				B:						
Pressure:	A:				B:				Control Frequency:		
Temp:	A:				B:						
For 49C:										(Also for 1008):	
Intensity:	A:				B:				Temperature:		
Noise:	A _{ref}		A _{sa} m		B _{ref}		B _{sa}				
Pressure:									Pressure:		
Bench:											
Bench lamp:											

COMMENTS

Form 2
O₃ Audit Form

SITE _____ **AUDITOR** _____

DATE _____ **LAST AUDIT** _____ **TEMP** _____ °C

AUDIT START TIME _____

ANALYZER BRAND/MODEL _____ **SN** _____

POT. ZERO _____ **SPAN/GAIN** _____ **RANGE** 0-.500/0-1.00 PPM

ROTAMETER SETTING(s) _____ **CAL. DATE** _____

PRIMARY RECORDER _____ HYUNDAI / DASIBI / SAMSUNG / ESC /

SECONDARY RECORDER _____ YOKAGAWA / EAMS /

DVM _____ FLUKE **Comments:** _____

AUDIT STD BRAND/MODEL _____ **SN** _____

CERT. DATE _____ **TOTAL FLOW** _____ L/M

STD CONCENTRATION = _____ X (INDICATED O₃ _____)

***ZERO RESPONSE(s)** PRIM. _____ SEC _____ DVM _____ STD Z _____

VALIDATION (.350-.450) POINT SET _____ READS _____

RESPONSE(s) PRIM _____ SEC _____ DVM _____

MEASURED _____ STD _____ %DIF _____

ACCURACY (.150-.200) POINT SET _____ READS _____

RESPONSE(s) PRIM _____ SEC _____ DVM _____

MEASURED _____ STD _____ %DIF _____

PRECISION (.080-.100) POINT SET _____ READS _____

RESPONSE(s) PRIM _____ SEC _____ DVM _____

MEASURED _____ STD _____ %DIF _____

ACCURACY (.030-.080) POINT SET _____ READS _____

RESPONSE(s) PRIM _____ SEC _____ DVM _____

MEASURED _____ STD _____ %DIF _____

AUDIT END TIME _____

REMARKS _____